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Hierarchical Structures Incorporating Carbon and Zeolite to Remove Radioactive Contamination

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Abstract

Synthesis, characterization and application of hierarchical zeolites are becoming a subject of an increasing interest among scientists and researchers. Hierarchical structures incorporating zeolites possess secondary porosity at meso- and macrolevel to overcome problem of mass transport, which occurs with using conventional zeolites.

In this study, the porous carbon surface was prepared by carbonization of the locally available agricultural waste of the Iraqi Nut shell (NS) using a carbonization method in a tubular furnace at 900˚C for two hours. Hierarchicalpours structures including zeolite were prepared by the mechanical activation of the carbon surface using ultrasonication with a nanoparticles suspension of ground commercial zeolite type 4A. Zeolite was milled using 0.3-0.4 mm diameter glass balls as grinding media to prepare nanoparticles seeding, which increases the crystallization of the amorphous aluminosilica gel on the modified carbon surface during the hydrothermal method. The Product of the syntheses of zeolite 4A and the hierarchal composite material were characterized using X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Nitrogen-Adsorption /desorption isotherms (BET), Energy Dispersive Spectroscopy (EDX), and Thermo Gravimetric Analysis (TGA) to determine the structure, morphology, surface area, chemical composition, and percentage weight of zeolite on carbon, respectively. The products were applied to remove the radioactive hazardous cesium isotope Cs^{137} from the radioactive wastewater provided by the destroyed building of Radiochemistry laboratories (RCL) in AL-Tuwaitha Nuclear Site. Gamma spectroscopy system with high purity germanium detector (HPGe) was used to measure the activity concentration for the contamination water before and after the treatment. The results showed that the activity concentration decreased from 4800 Bq/L to 186Bq/L and 100Bq/L using pure zeolite 4A and NSZ.respectively. The results also showed that the composite materials could be used effectively to remove radioactive ^{137}Cs from a real wastewater, with ease of separation and recovery from the solution compared with the pure zeolite 4A.

Keywords: Hierarchical structures, zeolite, carbon, radioactive waste, cesium^{137}Cs

تراكيب سُلميه تتضمن الكربون والزيولايت لإزالة التلوث الأشعاعي

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الخلاصة

أصبحت عملية تصنيع،وتشخيص وتطبيق المواد السُلمية المحتوية على الزيولايت أحد المواضيع التي نالت الاهتمام المتزايد من قبل العلماء والباحثين. تمتلك التراكيب السُلميه التي تتضمن الزيولايت مسامات ثانويه ميزو – ماكرو للتغلب على مشكلة نقل الكتله المترافق مع استخدام الزيولايت التقليدي.في هذه الدراسة ، تم إعداد سطح الكربون المسامي بواسطة عملية تفحيم للنفايات الزراعية المتوفرة محليًا قشور الجوز (NS.) وذلك باستخدام طريقة الكربنة في فرن انبوبي عند $900^{\circ}C$ لمدة ساعتين.يتم تحضير تراكيب سُلمية مسامية متضمنة الزيولايت بواسطة التنشيط الميكانيكي لسطح الكربون باستخدام الموجات فوق الصوتية لمحلول غروي يحتوي على دقائق نانوية للزيولايت التجاريمن نوع 4A.

وقد تم طحن الزيولايت التجاري باستخدام كرات زجاجية بقطر (0.3–0.4 mm) كوسيط للطحن لتحضير بذرات الدقائق النانوية التي تزيد من تبلور جل الزيولايت غير المتبلور على سطح الكربون المنشط ميكانيكياً أثناء طريقة الهايدروثيرمل. تم تشخيص الزيولايت المحضر(4A) والمواد السُلمية المتراكبة المحضرة باستخدام (XRD,SEM,BET,EDX and TGA) للتحقق من البنية البلورية وهيئة السطح والمساحة السطحيه والتركيب الكيميائي ونسبة الزيولايت المحمل سطح الكربون على التوالي. تم تطبيق هذه التراكيب لإزالة نظير السيزيوم المشع Cs^{137} من المياه الملوثة اشعاعيا والتي تم جلبها من بناية مختبرات الكيمياء الإشعاعية المدمرة (RCL)في موقع التويثة النووي. استخدمت منظومة أطياف كاما المزودة بكاشف الجرمانيوم عالي النقاوة (HPGe) لقياس تركيز النشاطية الإشعاعية للمياه الملوثة قبل وبعد المعالجة.

اظهرت النتائج ان المادة المتراكبة يمكن استعمالها وبشل كفؤ لأزاله السيزيوم المشع مع سهولة الفصل من المحلول مقارنة مع الزيولايت الصناعي المحضر نوع 4A.

1. Introduction

During the past several years, different types of hierarchal structured zeolitec materials have been synthesized due to their highly attractive properties, including high mass transfer, low-pressure drop, and high surface area [1].Zeolites are nonporous, crystalline materials that have been widely used in many fields, such as detergence, petroleum industry, wastewater treatment, pharmaceutical and environmental protection [2].

Zeolite materials are found in nature and they can be synthesized in the laboratory. The crystal structure of this inorganic material consists of SiO_4 and AlO_4 tetrahedral with oxygen atoms connecting the neighboring tetrahedral. The structure of zeolite contains cavities and channels of molecular dimensions [3]. The sizes and shapes of the pores as well as the cavities vary depending on the zeolite structure type [4]. Much of the success of zeolites in many applications like catalysis and ion - exchange can be ascribed to the presence of the micropores. Diffusion limitations due to the restricted access and slow mass transport to and from active sites located within the micropores represents the major drawback in most industrial reactions catalyzed by zeolites.

The term hierarchal porous strictures refers to a range of materials having two or more porosity levels which have been adapted to overcome diffusion problems and mass transfer resulting from binding and pelletizing of zeolite [5].

Typically, hierarchical zeolites are made either by templating methods or by post –syntheses modification (delamination, desilication) and controlled crystallization [6]. Different authors prepared a variety of zeolitic hierarchical structures using different types of zeolite. Hernandez-Ramirez *et al.* [7] prepared hierarchically structured zeolite Y over carbonized olive seeds and coconut shells and fibres using a seeding process coupled with ultrasonication.

In this study, novel structures consisting of carbon coupled with Linda type 4A zeolite were synthesized to enhance mass transfer and increase surface area. The target zeolite should be added as seeds for the sonicated carbon samples to increase the crystallization rate. Al-Nasri [8] and Sama *et al.* [9] studied the effects of nanoparticle seeds on preparation of hirerically porous structures. The authors found that the using of seeding on the temples surface induced crystallization of the amorphous aluminosilicat during the hydrothermal treatment.

2. Experimental Part

2.1 Materials

In order to prepare the synthesized material of zeolite A , the following raw materials were used without any additional purification: Sodium aluminate(50%Al_2O_3 , sigma Aldrich) as alumina source, sodium metasilicate ($Na_2.SiO_3.9H_2O$, BDH) as a silica source, and sodium hydroxide (99.9%) as mineralizing agent, while carbonaceous supports were prepared from available agricultural waste (Iraqi Nutshells) by a thermal treatment.

2.2 Zeolite 4A Synthesis

Zeolite 4A was synthesized by dissolving silica and alumina in alkaline solution according to the formula [10]:$3.1Na_2O:Al_2O_3:1.9SiO_2:12H_2O$. NaOH (0.94g) was added to 30g deionized water , and this solution was then split into two equal halves. To the first half, sodium aluminate (3.22g) was added and mixed until clear solution was obtained. To the second solution, sodium silicate (2.43g) was added and mixed for 15 min. Both precursors were mixed together and stirred for 30 min. Aluminosilical gel was then transferred to a stainless autoclave lined with Teflon land. Zeolite 4A was crystallized at 100°C for 2 and 4 h. The product was then filtered, washed with deionized water until the pH of the outer water was <9, and then dried at 80C for 6 h. The powder was then collected and characterized by X-ray diffraction (XRD), scanning electron Microscopy (SEM), N_2-Adsorotion / desorption isotherms and Energy Dispersive Spectroscopy (EDAX) in order to measure structure , morphology, surface area and the chemical composition for the product.

2-3 Preparation of Carbon Support Materials

The raw materials used to prepare carbon were inexpensive and available agricultural waste (Iraqi nut shell and palm tree)> They were collected from a local shop, washed, dried and then weighted before entering a tubular furnace at 900C for 2h. Nitrogen gas flow was applied through the furnace, and the prepared carbon was weight and ground manually to obtain carbon powder with a particle size of 60-600µm. SEM image was taken to this sample to illustrate the morphological structure of carbon.

2-4 Ball Mill Technique

Commercial zeolite 4A was used to prepare nanoparticles suspension as seeding on carbon surface to increase crystallization rate. 0.3-0.4mm diameter glass beads were used as grinding media according to the following weight ratio: 1H20: 1zeolite4A: 2 grinding media. The product was finally characterized by Dynamic Light Scattering (DLS) to measure the particle size of suspension.

2-5 Preparation of Hierarchal Structures

To modification of the surface of carbon and the induction of growth of zeolite crystals on the seeded carbon was performed for samples consisting of carbon: suspension nanoparticles (mass ratio 15:1) using ultrasonication path for 6h.

Hierarchal composite of zeolite 4A over the nut shell carbon was prepared hydrothermally by adding carbon to aluminosilical gel. The carbon support was used in the ratio of 2:1carbon to silica available in the silica source with mixing for 10 min. Then, the gel was placed in Teflon – lined autoclave and heated in an oven for 4 h. After that, the product composite was filtered, washed with deionized water until pH <9, and characterized by XRD, SEM, EDAX, ,TGA and N2- adsorption/desorption isotherm.

3. Results and Discussion

3.1 Characterization

The x-ray diffraction patterns of the prepared zeolite and composite materials are shown in Figure-1, where the pattern shows the plot of the x-ray intensity diffraction from the sample versus thediffraction angle (Brage) 2Ɵ.

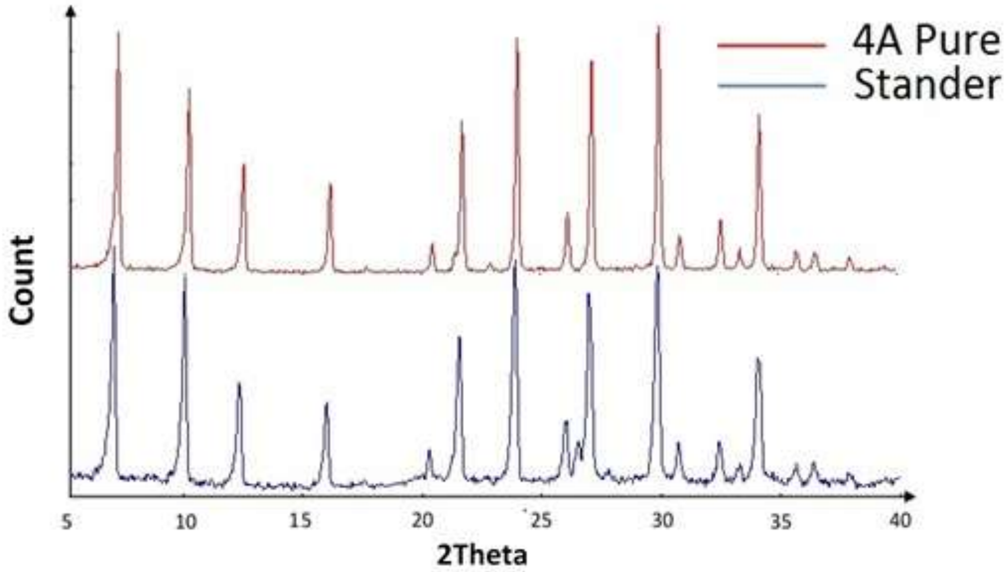

Figure 1-X-ray diffraction of the prepared Zeolite 4A.

From the X-ray diffraction patterns, it can be observed that the prepared zeolite has a good crystallinity, where the crystals nearly have the same structure as the standard type and that the crystallization of the samples were successfully completed. The X-ray diffraction of the prepared 4A has a small peak at angles (2θ = 7°) and (2θ = 10°), while the characteristic angle was at (2θ = 30°) [11].

The X-ray patterns from the two composite materials (Figure-2 were compared with those from the pure zeolite 4A sample, which showed that the presence of natural carbon does not affect the synthesis process of zeolite.

The morphology structure of the prepared carbon is shown in Figure-3 (a,b). SEM images of the carbonized materials illustrate the porous surface which found in the nutshell's carbon. The morphology of the prepared zeolite 4A is shown in SEM images (b,c) from the same figure. SEM images revealed the good crystallization of the prepared zeolite 4A, with a cubic shape and approximately 2µm particle size.

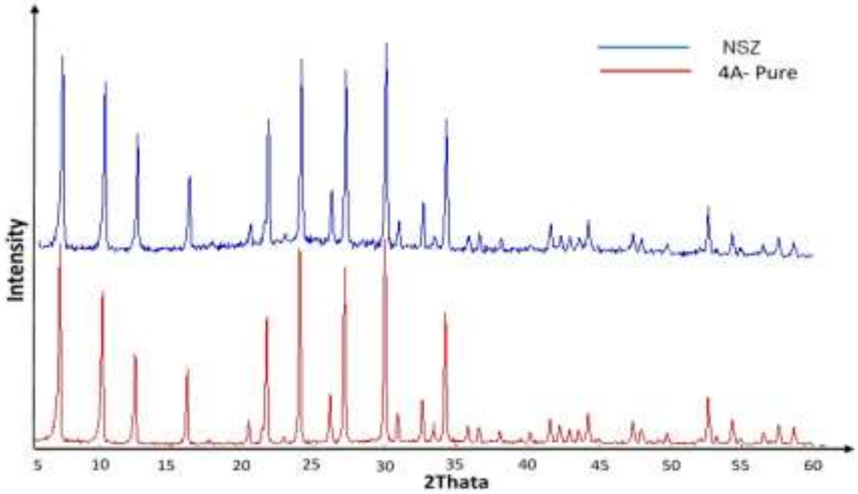

Figure 2-XRD patterns of pure zeolite 4A and composite zeolite 4A prepared using nutshell carbon.

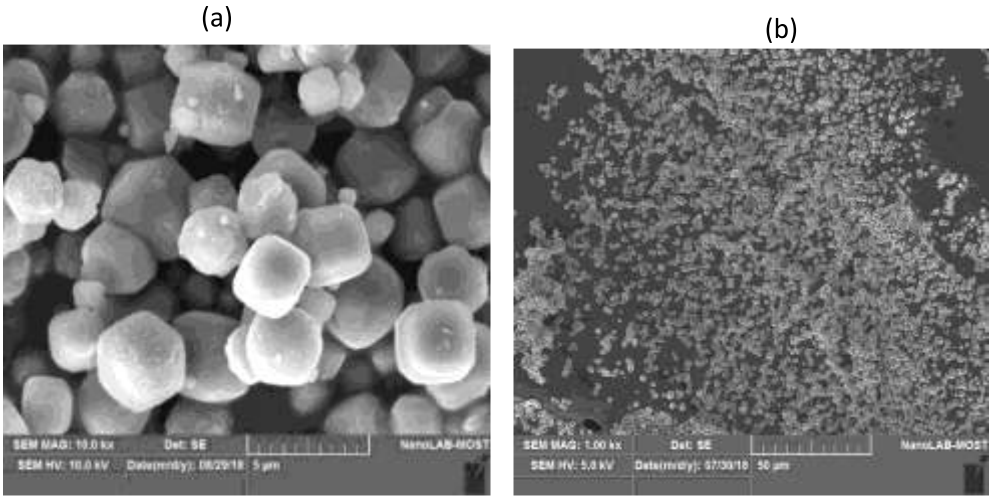

Figure 3-SEM images in different magnifications for nutshells carbon (a,b) and zeolite 4A (c,d).

(c) (d)

The SEM images of zeolite 4A composite, prepared using NS and PD carbons ultrasonicated in the presence of zeolite A nanoparticles, are shown in Figure-4. The SEM images show fully crystallized and uniformly shaped crystals with a good distribution over the carbon surface.

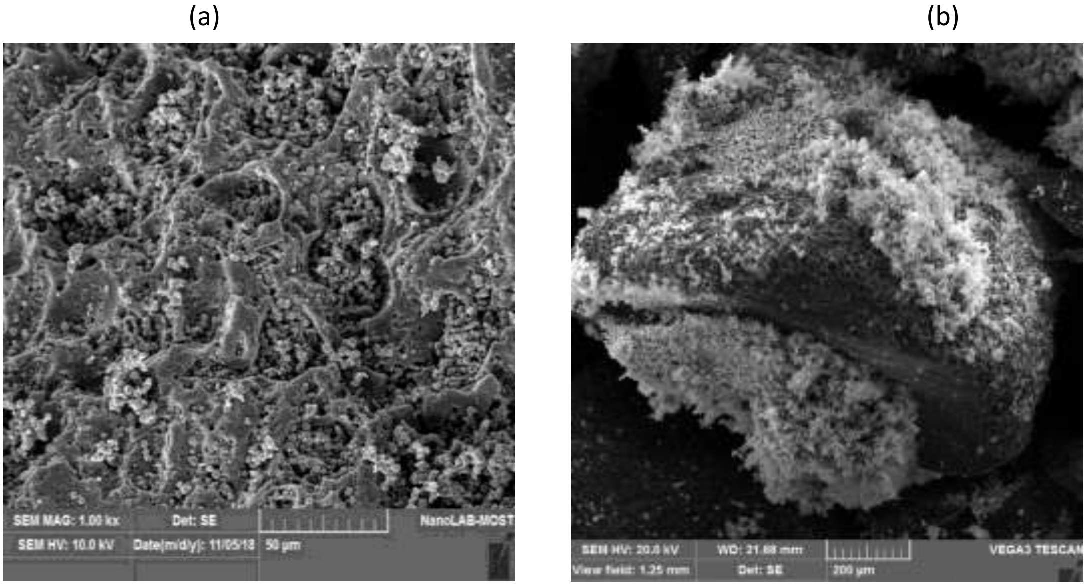

Figure 4-SEM images of nutshells carbon with 4A composite in different magnifications

The fine particle size of zeolite crystals was obtained from a commercial zeolite 4A, which was ground via wet ball milling. The average particle size of the crushed zeolite 4A was found using the Dynamic Light Scattering (DLS) technique. The suspension of fine particles of zeolite with an average particle size of 260 nm was fixed to the organic scaffolds using ultra sonication agitation for 6h.

Energy Dispersive Spectroscopy (EDAX) technique was used for pure zeolite 4A and hierarchal composite samples to evaluate the ratio between silicon and aluminum. Figure-5 shows that the Si/Al ratio was >0.97 and 0.90 for pure zeolite 4A and NSZ, respectively. The ratio was about 1, which is the ratio between silicon and aluminum in zeolite type A, which agrees with previous results [11, 12].

Surface area was determined using the Brunauer-Emmett-Teller (BET) method for the zeolites and composites samples. The results of surface area are shown in Table-1

Table 1-The Surface area results

Sample	Surface area m^2/g
Pure 4A	19.1037
Nut Shell carbon	404.0558
NSZ.Cpmposite	207.9485

The percentage loading of zeolite on carbon surface was determined using the thermogravimetric analysis (TGA) for the hierarchal composite sample. It was found from the results of (TGA) that the percentage loading of zeolite on carbon surface was 40%.

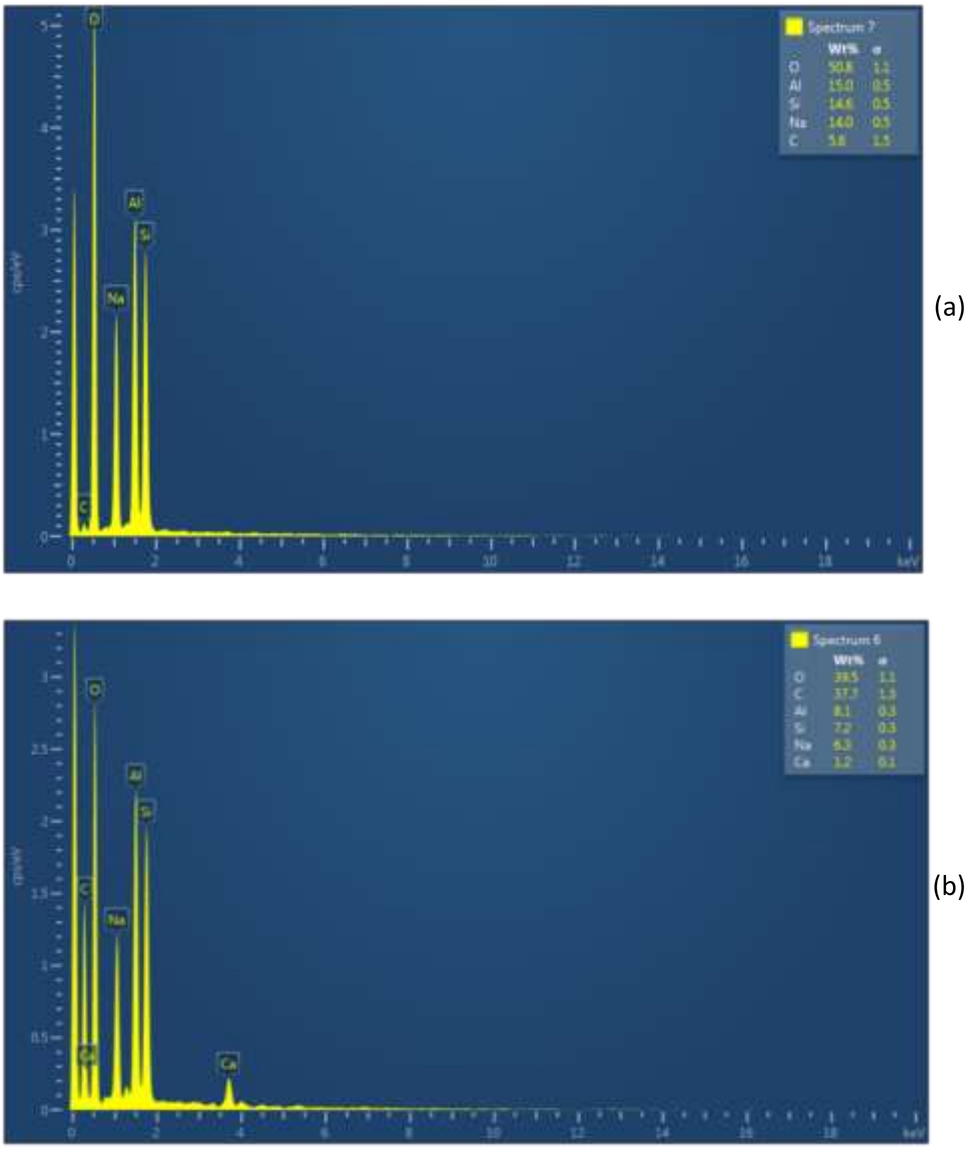

Figure 5-EDX analysis results. (a) 4A pure (b) NSZ.

3.2 Application of the Hierarchal Composite with a Real Radioactive Solution

The prepared hierarchal composite NSZ was applied to remove the radioactive ^{137}Cs from wastewater collected from the destroyed building of Radio Chemistry Laboratories (RCL) in Al-Tuwaitha Nuclear Site. Gamma spectroscopy (Canberra), supplied by high purity germanium detector (HPGe) with 60% relative efficiency, was used to measure the activity concentration for the liquid waste before and after the treatment. Batch mode was performed using 20 ml of the contaminated solution mixed with different weights of the absorbent materials. The contact time was three hours, the initial activity concentration was 4800Bq/L, while the pH of the solution was 6.5 in room temperature.

3.3 Treatment Results

Different weights of the pure zeolite 4A and the hierarchal structure NSZ were used to remove radio cesium from wastewater. Figure-6 shows that the activity concentration of the liquid waste was decreased significantly with increasing the weight of the absorbent material. Figure-7 illustrates that the removal efficiency (R%) for cesium was increased with increasing the weight for both 4A zeolite and NSZ.

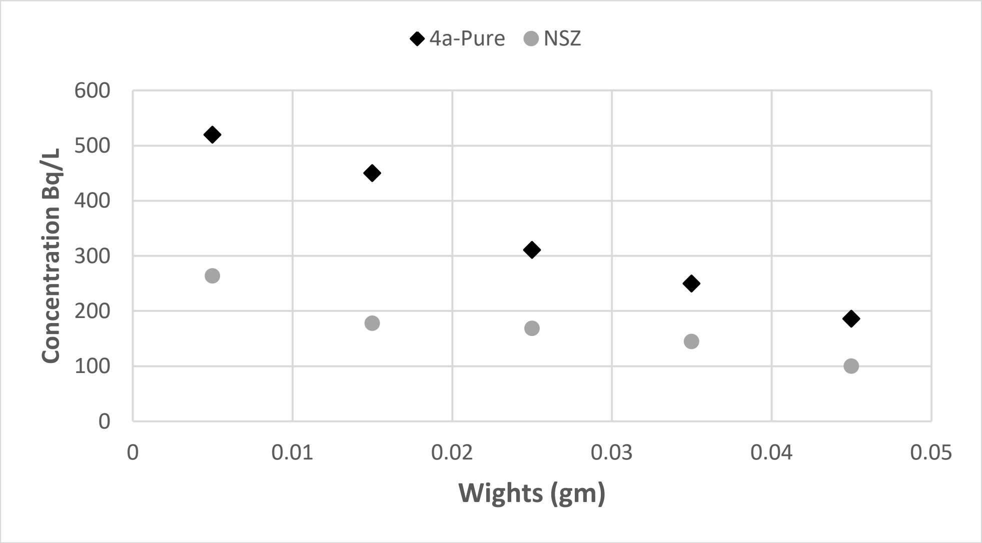

Figure 6-The effect of adsorbent weight on activity concentration. The initial activity concentration of cesium -137 was 4800Bq/L , PH=6.5 at room temperature.

Conclusions

Zeolite -4A , hierarchal structure incorporating zeolite, and carbon were successfully synthesized using hydrothermal method from amorphous gel. Porous carbon surface was prepared using locally available agricultural waste (Nutshell) by carbonization method in a tubular furnace at 900˚C for 2h. Then, the carbon surface was activated using ultrasonication in a suspension containing fine particles of commercial zeolite 4A to induce the crystallization process.

The characterization using X-Ray diffraction showed that the XRD patterns of the prepared zeolite and DMZ composite has the same crystalline structure of the commercial zeolite A. The porous carbon is withstanding and not affecting the structure of zeolite during the hydrothermal method, which makes it preferred as a scaffold material in hierarchal structures. The BET surface area increased from 19.103 m^2/gm to 207.9485 m^2/gm for the synthesized zeolite 4A and NSZ composite, respectively. The prepared zeolite A and DMZ composite were applied to remove the ^{137}Cs isotope from a real radioactive wastewater sample collected from Radiochemistry Laboratories in Al-Tuwaitha nuclear site.

The radioactivity of ^{137}Cs decreased from 4800Bq/L to186 Bq/L and 100 Bq/L by using 0.045 gm from both materials. The results show that the composite material could be used effectively as an eco-friendly agent to remove the radioactive isotopes from the contaminated wastewater.

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